Direct observation of mixing of spin multiplets in an antiferromagnetic molecular nanomagnet by electron paramagnetic resonance

S. Datta, O. Waldmann, A. D. Kent, V. A. Milway, L. K. Thompson, and S. Hill
1Department of Physics, University of Florida, Gainesville, Florida 32611, USA
2Department of Chemistry and Biochemistry, University of Bern, CH-3012 Bern, Switzerland
3Department of Physics, New York University, 4 Washington Place, New York, New York 10003, USA
4Department of Chemistry, Memorial University, St. John’s, Newfoundland A1B 3X7, Canada
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High-frequency electron paramagnetic resonance (EPR) studies of the antiferromagnetic Mn-[3 × 3] molecular grid clearly reveal a breaking of the ∆S=0 selection rule, providing direct evidence for the mixing of spin wave functions (∆ mixing) induced by the comparable exchange and magnetoanisotropy energy scales within the grid. This finding highlights the potential utility of EPR for studies of exchange splittings in molecular nanomagnets, which is normally considered the sole domain of inelastic neutron scattering, thereby offering improved sensitivity and energy resolution.

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The synthesis of ordered crystalline arrays (ensembles) of nominally identical magnetic molecules has enabled unprecedented insights into quantum magnetization dynamics at the nanoscale, leading to exciting discoveries such as the quantum interference associated with the coherent rotation (tunneling) of a large spin.1 The molecular approach is particularly attractive due to the highly ordered and monodisperse nature of the molecules in the solid state and because one can systematically vary many key parameters that influence the quantum behavior of a magnetic molecule, e.g., the total spin, symmetry, etc. The magnetism of these molecules can be described quite generally by the microscopic spin Hamiltonian,2

\[ \hat{H} = - \sum_{ij} J_{ij} \hat{S}_i \cdot \hat{S}_j + \sum_i \hat{s}_i \cdot D_i \cdot \hat{s}_i + g \mu_B \hat{S} \cdot B. \]  (1)

The first term parametrizes the Heisenberg interaction between each pair of magnetic ions; \( \hat{S}_i \) are the spin operators at each site, and \( J_{ij} \) the respective coupling constants. The second term accounts for the magnetic anisotropy at each site; \( D_i \) are the local zero-field-splitting (ZFS) tensors. The final term is the Zeeman interaction written in terms of the total spin operator \( \hat{S} \).

In the strong exchange limit, the total spin \( S \) is a good quantum number and the exchange term splits the energy spectrum into well separated spin multiplets, each having comparatively weaker ZFS due to magnetic anisotropy.3 However, as the ZFS increases relative to the exchange splitting, mixing of spin multiplets becomes significant (\( S \) mixing) such that \( S \) no longer constitutes a good quantum number.4,5 This parameter regime has attracted growing interest due to the realization that \( S \) mixing plays a crucial role in the quantum dynamics of coupled spin systems, namely, in the tunneling terms in single-molecule magnets (SMMs) and antiferromagnetic (AF) clusters,6–9 and in the novel magneto-oscillations associated with the total spin of a molecule.10–12 Indeed, the interplay between anisotropy and exchange is central to the understanding of (nano)magnetism, and experimental determination of exchange and anisotropy splittings is of great value.

ZFS caused by magnetic anisotropy may be studied spectroscopically using both electron paramagnetic resonance (EPR) and inelastic neutron scattering (INS). In contrast, the most unambiguous method for estimating exchange couplings involves determining the exact locations of excited spin multiplets. For this reason, such investigations have been limited to INS since the EPR selection rule \( \Delta S=0 \) forbids excitations between spin multiplets (the INS selection rule \( \Delta S=0, \pm 1 \) permits such intermultiplet transitions). In this work, we show that \( S \) mixing indeed can give rise to a situation in which exchange splitting is observed directly in a nanomagnet using high-sensitivity multi-high-frequency EPR.

The Mn-[3 × 3] grid is an attractive candidate in the above context. Its structure consists of nine spin-\( \frac{5}{2} \) Mn\(^{II} \) ions placed at the vertices of a \( 3 \times 3 \) matrix, see Fig. 1(a). A significant magnetic anisotropy, demonstrated in previous experiments,13 gives rise to several striking effects, including novel quantum oscillations in the field dependent magnetic torque,10 and tunneling of the Néel vector at high fields.14 The magnetism of Mn-[3 × 3] can be well described by the approximate Hamiltonian,

\[ \hat{H}_1 = - J_R \left( \sum_{i=1}^{7} \hat{s}_i \cdot \hat{s}_{i+1} + \hat{s}_8 \cdot \hat{s}_1 \right) - J_C \sum_{j=1}^{4} \hat{s}_j \cdot \hat{s}_9 + D_R \sum_{i=1}^{8} \hat{s}_{i,z}^2 + D_C \hat{s}_{9,z}^2 + g \mu_B \hat{S} \cdot B, \]  (2)

with AF couplings \( J = J_R = J_C < 0 \) and uniaxial easy-axis anisotropy \( D = D_R = D_C < 0 \) (spins are numbered according to Fig. 1; \( z \) denotes the axis perpendicular to the grid).10 Here, we report the clear observation of an EPR transition between the \( S=\frac{5}{2} \) ground state and the first excited \( S=\frac{3}{2} \) spin multiplet, i.e., a \( \Delta S=\pm 1 \) transition.

The observation via EPR of intermultiplet transitions for a molecular nanomagnet is of significance from at least three points of view.

(1) It demonstrates that with today’s EPR spectrometers,
it is possible to directly measure exchange splittings. This represents a significant development, with the potential to change the landscape of experiments on exchange coupled systems. EPR offers many advantages compared to INS, such as high sensitivity (much smaller single crystals), “cheap” experimental environments, essentially unlimited spectral resolution permitting linewidth studies, etc.

(2) To date, the most direct evidence for S mixing has involved measuring energy spacings in EPR and INS spectra, and then comparing these to calculations.\(^{8,12}\) In the present case, however, evidence comes from the observation of an otherwise forbidden EPR transition, i.e., breaking of the selection rule \(\Delta S=0\)—a property directly related to the wave functions. This is, hence, the most clear-cut experimental demonstration of S mixing.

(3) Mn-[3 \(\times\) 3] was the first molecule in which the effects of S mixing were clearly demonstrated, and subsequent studies have shown that the generic Hamiltonian \(\hat{H}_I\) provides a complete description of these effects.\(^{10}\) The present EPR results confirm these findings and provide textbook quality insights into the physics of magnetic molecules and the effects of S mixing.

Single crystals of Mn-[3 \(\times\) 3], \([\text{Mn}_{n}(2\text{POAP}-2\text{H})_6]\) \(\times\) (ClO\(_4\))\(_6\) \(\cdot\) 3.57MeCN\(\cdot\)H\(_2\)O, were prepared as reported.\(^{15}\) They crystallize in the space group C\(_2\)\(\cap\)c. The cation \([\text{Mn}_{n}(2\text{POAP}-2\text{H})_6]\)\(^{6+}\) exhibits a slightly distorted \(S_4\) symmetry, with the \(C_2\) axis perpendicular to the grid plane and parallel to the uniaxial magnetic easy (\(z\)) axis. Single-crystal EPR spectra were obtained using a sensitive cavity perturbation technique. A vector network analyzer was used to record the complex signal (amplitude and phase) transmitted through the cavity; this technique is described in detail elsewhere.\(^{16}\) Data were recorded for two samples. If not otherwise stated, the magnetic field was applied along the \(z\) axis.

Figure 1(a) displays the 62 GHz EPR spectrum obtained at 1.4 K. Five transitions labeled \(P_n\) \((n=1,2,3,4,5)\) are clearly observed. \(P_1\) is the \(M_\|=\frac{1}{2}\rightarrow +\frac{1}{2}\) signal expected for a half-integer spin system and will not be discussed in detail. The temperature dependence of the 52 GHz EPR spectrum is shown in Fig. 2. Upon increasing the temperature, additional transitions appear, e.g., \(P_4\), \(P_5\), and the rich fine structure around \(P_3\), which is of no interest in this work. Above \(\sim 20\) K, only a central line is observed, which is expected due to the thermal population of a large number of spin multiplets with negligible ZFS. In Fig. 1(b), we display the frequency dependence of the resonance fields \(B_n\) of the peaks \(P_n\) \((n=1,\ldots,5,\ldots)\); each depends linearly on frequency due to the Zeeman term in Eq. (2). The ZFS may be obtained from the \(B=0\) intercepts by extrapolation. \(B_1\) to \(B_5\) increase with frequency; in contrast, \(B_d\) decreases with frequency as also seen from the sense of the phase rotation through the resonance [Fig. 1(a)]. A clear hint that \(P_d\) is not a usual intramultiplet transition \((\Delta S=0)\) is found from the large \(B=0\) offset of \(\sim 233\) GHz. ZFS caused by magnetic anisotropy is much smaller for Mn\(^{II}\) complexes.\(^{17}\) This suggests that the large offset for \(P_d\) is caused by exchange, i.e., \(P_d\) is an intermultiplet transition. Furthermore, previous magnetic and INS measurements determined the zero-field gap between the \(S=\frac{5}{2}\) ground and first excited \(S=\frac{7}{2}\) states to be 230\(\pm\)10 GHz,\(^{10,13}\) thus suggesting that \(P_d\) indeed corresponds to the \(S=\frac{5}{2}\rightarrow \frac{7}{2}\) transition.

Before discussing \(P_d\) further, we focus on the analysis in terms of \(\hat{H}_I\), with the aim to obtain best-fit values for \(J\) and \(D\). In a first step, we fit straight lines to the data in Fig. 1(b) with a common \(g\) factor, yielding values for the ZFS associated with each transition (see Table I) and \(g=1.970(7)\). We then determine \(J\) and \(D\) as follows. A least-squares fit based on the full Hamiltonian would be very demanding because its dimension is \(10\ 077\ 696\). However, it has previously been demonstrated that the energies and wave functions of the low-lying states of relevance here can be

![Figure 1](image1.png)

**FIG. 1.** (Color online) (a) Complex EPR spectrum at 1.4 K and 62 GHz. The dips in amplitude correspond to EPR; the sense of phase rotation through each dip differentiates \(\Delta M=\pm 1\) transitions. The Mn-[3 \(\times\) 3] grid is shown in the inset. (b) Frequency dependence of the resonance fields \(B_n\) of the indicated peaks; the solid lines represent best fits (see text).

![Figure 2](image2.png)

**FIG. 2.** (Color online) Temperature dependence of the EPR spectrum at 52 GHz; several of the transitions have been labeled. The inset shows the temperature dependence of transition \(P_d\).
TABLE I. First line: Experimental ZFS determined from fits to the data in Fig. 1(b). Second line: Calculated ZFS using the best-fit $J$ and $D$ values. Energies are given in GHz.

<table>
<thead>
<tr>
<th>$P_1$</th>
<th>$P_2$</th>
<th>$P_3$</th>
<th>$P_4$</th>
<th>$P_5$</th>
<th>$P_d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>42.7(3)</td>
<td>24.3(4)</td>
<td>13.2(5)</td>
<td>4.4(5)</td>
<td>−23.3(7)</td>
<td>233(1)</td>
</tr>
<tr>
<td>42.80</td>
<td>24.47</td>
<td>12.62</td>
<td>3.79</td>
<td>−24.47</td>
<td>233.0</td>
</tr>
</tbody>
</table>

Calculated with high accuracy from the effective spin Hamiltonian $\hat{H}_1=−0.526J_{\beta}S_\beta\hat{A}_\beta+J_2S_\beta\hat{A}_\beta \cdot \hat{S}_\beta+0.197D_\beta(S_\beta^2+S_\beta^2)+D_{\chi\alpha\beta}g\mu_B\hat{S}_\beta \cdot \hat{B}$.\textsuperscript{14} $A$ ($B$) denotes the sublattice of corner (edge) spins [see Fig. 1(a)], i.e., $\hat{S}_\alpha=\hat{S}_1+\hat{S}_2+\hat{S}_3+\hat{S}_4$, $(\hat{S}_\beta=\hat{S}_2+\hat{S}_4+\hat{S}_5+\hat{S}_6)$. The dimension of $\hat{H}_1$ is only 2646, permitting a true least-squares fit to the data. We obtain $J=−4.76(4)$ K and $D=−0.144(2)$ K, in very good agreement with previous experiments.\textsuperscript{10,13} The calculated ZFS values are compared to the experiment in Table I; the agreement is excellent.

From a general point of view, our model for Mn-[3 × 3] appears oversimplified. Even if one assumes ideal symmetry, the exchange and anisotropy parameters need not be identical for all Mn$^{2+}$ ions in the Mn-[3 × 3] grid. Indeed, evidence for slight variations in the exchange constants was inferred from INS studies.\textsuperscript{13} However, no variation was found from the present measurements or from thermodynamic studies.\textsuperscript{10} This is because the relevant energies are governed by the average of the exchange constants; hence, only a single $J$ is needed. Similar arguments apply to the anisotropy parameters and, in fact, no evidence for a variation has been reported so far. Consequently, the generic Hamiltonian $\hat{H}_1$ (or $\hat{H}_2$) with just the three parameters, $J$, $D$, and $g$, captures all of the relevant physics and provides an excellent effective description of the low-energy properties of Mn-[3 × 3]. The EPR results presented here establish the most critical test so far.

The calculated low-energy, low-field spectrum for Mn-[3 × 3] is displayed in Fig. 3(a). It consists of an $S=\frac{3}{2}$ ground state and a first excited $S=\frac{5}{2}$ multiplet; these are further split into three and four $\pm M$ sublevels, respectively. In zero field, the $M=\pm \frac{5}{2}$ ($\pm \frac{3}{2}$) levels of the $S=\frac{5}{2}$ ($S=\frac{3}{2}$) multiplet lie lowest in energy due to the easy-axis anisotropy. The $\pm M$ sublevels split in magnetic field due to the Zeeman interaction. The $M=−\frac{5}{2}→−\frac{3}{2}, M=−\frac{3}{2}→−\frac{1}{2},$ and $M=\frac{1}{2}→\frac{3}{2}$ transitions within the $S=\frac{3}{2}$ multiplet give rise to $P_1$, $P_2$, and $P_5$, respectively. Hence, the ZFS for $P_2$ and $P_5$ should be equivalent in magnitude but opposite in sign, in agreement with the observation (see Table I). Peaks $P_3$ and $P_4$ correspond to the $M=−\frac{3}{2}→−\frac{1}{2}$ and $M=−\frac{5}{2}→−\frac{1}{2}$ transitions within the $S=\frac{5}{2}$ multiplet. As already noted, $P_3$ corresponds to the transition between the $M=−\frac{5}{2}$ level of the $S=\frac{5}{2}$ multiplet and the $M=−\frac{1}{2}$ level of the $S=\frac{5}{2}$ multiplet. The observed temperature dependence (Fig. 2) is perfectly consistent with these assignments.

In the inset to Fig. 3(b), we display the field orientation dependence of $B_d$ at several frequencies. Agreement between experiment (open squares) and theory (solid curves) is very good, including the opposing trends at lower and higher frequencies and/or fields. This behavior can be traced to the level repulsion ($S$ mixing) between the $S=\frac{5}{2}, M=−\frac{3}{2}$ level and various $S=\frac{3}{2}$ states as the field is tilted away from the symmetry direction of the Mn-[3 × 3] grid. As such, this nonlinear frequency dependence of $B_d$ represents evidence for quantum spin-state oscillations.\textsuperscript{12}

According to the above, $P_d$ violates the $\Delta S=0$ selection rule for EPR. However, labeling levels by $S$ can be misleading because of strong $S$ mixing. In fact, $S$ is no longer a good quantum number, though we retain the notation as a matter of convenience. In order to rigorously check the peak assignments, we performed a full simulation of the EPR spectrum. Results for 62 GHz are shown in Fig. 3(b) at two temperatures. The agreement with experiment is once again excellent. Most importantly, the calculations confirm the significant intensity of $P_d$. Hence, the mixing of spin multiplets is strong enough in Mn-[3 × 3] to observe $P_d$ using state-of-the-art high-frequency EPR techniques ($P_6$ is not observed experimentally due to its ten times lower calculated intensity). The wave functions of the two states involved in $P_d$ are calculated as \(0.986][\frac{1}{2},−\frac{3}{2})+0.162[\frac{1}{2},−\frac{5}{2})−0.034[\frac{3}{2},−\frac{5}{2})\) + \cdots and \(0.992[\frac{1}{2},−\frac{3}{2})−0.121[\frac{1}{2},−\frac{5}{2})+0.027[1,\frac{7}{2})+\cdots\)

(\text{with an $\{S,M\}$ notation for the basis functions). Hence, the ground state has 16% of $S=\frac{1}{2}$ admixed to it or 2.6% in squared (intensity) units.

In the strong exchange limit (\(|J| \gg |D|\)), the zero-field en-
Energies within each multiplet are expected to scale with $M$ as $M^2$. However, this behavior is strongly perturbed in Mn-[3×3], with the $M=\pm 3$ and $\pm 1$ states even occurring out of sequence for the $S=\frac{3}{2}$ multiplet. A standard approach involves the use of an effective spin Hamiltonian, $\hat{H}_S = D^0_{S} \hat{S}_z^2 + B^0_{S} \hat{O}_{\delta}^0$, to describe each spin multiplet. For an $S = \frac{3}{2}$ state, deviations from the expected $M^2$ behavior may be captured by the $B^0_{S}$ parameter (for larger $S$, higher order terms such as $B^0_{\delta} \hat{O}_{\delta}^0$ may be important also). It is the $S$ mixing that gives rise to significant $B^0_{S}$ values (and higher order terms), as noted in previous works.\textsuperscript{4,5,8} The ratio $|B^0_{\delta}/D|$, therefore, serves as a measure of the degree of $S$ mixing. For the $S=\frac{3}{2}$ multiplet in Mn-[3×3], it is $6.6 \times 10^{-4}$, and for $S=\frac{5}{2}$ it is $29 \times 10^{-4}$. For comparison, we list the values of $|B^0_{\delta}/D|$ for some of the lowest lying states of several other molecular clusters, which are considered to show $S$ mixing: 0.2×$10^{-4}$ for Fe$_4$ ($S=5$), 0.5×$10^{-4}$ for Mn$_{12}$ ($S=10$), 2×$10^{-4}$ for Ni$_4$ ($S=4$), and 5×$10^{-4}$ for the $S=2$ excited state of the ferric wheel CsFe$_8$.\textsuperscript{1,4,8,9} Apparently, Mn-[3×3] shows the strongest $S$ mixing. In principle, exchange constants may be determined indirectly using Eq. (1) on the basis of deviations from the expected $M^2$ behavior. However, this works only for the simplest systems, as recently demonstrated for a Ni$_4$ SMM.\textsuperscript{8} In the present work, the exchange splitting was determined by direct spectroscopy via EPR.

It is apparent that the effects of $S$ mixing become more important as the separation between spin multiplets decreases. This argument can, however, be misleading. For example, the $S=10$ ground and first excited $S=9$ multiplets overlap in Mn$_{12}$, yet $S$ mixing is relatively weak ($|B^0_{\delta}/D|=0.5 \times 10^{-4}$). In contrast, $S$ mixing is ten times stronger in Mn-[3×3], in spite of the fact that the $S=\frac{5}{2}$ and $\frac{3}{2}$ states are well separated in energy (see Fig. 3). Evidently, other factors must be important too, such as the spatial symmetries of the relevant spin wave functions.\textsuperscript{5} Therefore, one should be careful in judging the importance of $S$ mixing solely on the basis of the separation of spin levels or indeed on the ratio of $J$ and $D$. Understanding this issue is of great importance in terms of the design of future molecule-based magnets.

In summary, we present direct spectroscopic evidence for the mixing of spin wave functions in a Mn-[3×3] grid through the observation of an otherwise forbidden inter-spin-multiplet EPR transition. Detailed analysis in terms of a generic spin Hamiltonian provides tremendous insights into the combined effects of exchange and anisotropy in a prototypical molecular nanomagnet.

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2. Intramolecular dipolar interactions are not negligible but have similar effects to the single-ion anisotropy and are captured by the $S^2_{ij}$ terms. Thus, $D$ values should be understood as including both anisotropy contributions.


